

## Supporting Information

Table S1. Oxidatively Modified Residues in the D1, D2, CP43, and CP47 Proteins with 0 sec Irradiation.

Individual residues are listed along with the modifications observed. In some instances, different modifications were observed for the same residue on different peptides. For a complete list of oxidative modification types, the amino acids targeted, and mass modifications searched for in this study, see (34).

Key: aa, aldehyde addition (-32 amu); ca, carbonyl addition (+14 amu) cysh; cysteine hydroxyl (-16 amu); gam, Glu/Asp modificationn (-30 amu); go, general oxidation (+16 amu); stcb, serine/threonine carbonyl (-2 amu). Please note that these data were published previously in an examination of putative oxygen channels within PS II (30).

### Modified Protein Residues

**D1**  $^2\text{T}^{\text{a}}$  + stcb or go,  $^3\text{A}^{\text{a}}$  + go,  $^6\text{E}^{\text{a}}$  + gam,  $^7\text{R}^{\text{d}}$  + ca,  $^{17}\text{F}$  + go,  $^{18}\text{C}$  + cysh,

$^{130}\text{E}^{\text{c}}$  + go,  $^{133}\text{L}^{\text{b}}$  + go,  $^{135}\text{F}^{\text{c}}$  + go,  $^{239}\text{F}$  + go,  $^{241}\text{Q}$  + ca,  $^{242}\text{E}$  + gam

**D2**  $^{13}\text{K}$  + go,  $^{14}\text{D}$  + gam,  $^{15}\text{L}$  + ca,  $^{16}\text{F}$  + go,  $^{19}\text{M}$  + go,  $^{20}\text{D}$  + ca,  $^{21}\text{D}$  + gad,

$^{238}\text{P}$  + ca,  $^{239}\text{T}$  + go,  $^{242}\text{E}$  + gad,  $^{247}\text{M}^{\text{c}}$  + go,  $^{345}\text{E}$  + gad,  $^{347}\text{L}$  + go,  $^{349}\text{R}$  + ca

**CP43**  $^{27}\text{D}$  + go,  $^{28}\text{Q}$  + ca,  $^{29}\text{E}$  + gam,  $^{195}\text{D}$  + gam,  $^{196}\text{V}$  + ca,  $^{197}\text{R}^{\text{d}}$  + go,  $^{354}\text{E}^{\text{c}}$  + gam,  $^{355}\text{T}^{\text{c}}$  +

go,  $^{356}\text{M}^{\text{c}}$  + aa or go,  $^{357}\text{R}^{\text{c}}$  + ca or go,  $^{367}\text{E}$  + gam,  $^{368}\text{P}$  + go,  $^{369}\text{L}$  + ca,  $^{375}\text{L}$  + ca,  $^{376}\text{D}$  + gam,  $^{379}\text{R}$  + go,

$^{383}\text{D}^{\text{d}}$  + ca or gam,  $^{384}\text{I}^{\text{d}}$  + ca,  $^{385}\text{Q}^{\text{d}}$  + go,  $^{389}\text{E}^{\text{d}}$  + gam,  $^{460}\text{D}$  + go,  $^{461}\text{R}$  + ca,  $^{462}\text{D}$  + gam,  $^{463}\text{F}^{\text{d}}$  + go,  $^{464}\text{E}^{\text{d}}$  +

gam,  $^{469}\text{M}$  + go

**CP47**  $^{58}\text{Q}$  + go,  $^{60}\text{M}$  + go,  $^{327}\text{A}$  + go,  $^{329}\text{S}$  + go,  $^{330}\text{M}$  + go or aa,  $^{358}\text{R}$  + go,  $^{359}\text{M}$  + go or aa,  $^{360}\text{P}$  + go or ca,

$^{361}\text{T}$  + go,  $^{363}\text{F}^{\text{c}}$  + go,  $^{364}\text{E}^{\text{c}}$  + gam,  $^{365}\text{T}^{\text{c}}$  + go,  $^{374}\text{D}$  + gam,  $^{376}\text{I}$  + go,  $^{377}\text{V}$  + ca,  $^{378}\text{R}$  + go,  $^{393}\text{E}$  + gam,  $^{394}\text{Q}$  +

ca,  $^{398}\text{T}$  + go,  $^{423}\text{R}$  + ca,  $^{424}\text{A}^{\text{c}}$  + go,  $^{425}\text{Q}$  + ca,  $^{428}\text{E}$  + gam,  $^{484}\text{P}$  + ca,  $^{485}\text{D}$  + gam,  $^{486}\text{L}$  + go or ca,  $^{487}\text{D}$  +

gam,  $^{488}\text{V}$  + go,  $^{489}\text{Q}$  + ca

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<sup>a</sup>Not resolved in the *Thermosynechococcus vulcanus* structure (15)

<sup>b</sup>Buried residues not adjacent to cavities/channels identified using PYMOL (37)

<sup>c</sup>Buried residues adjacent to cavities/channels identified using PYMOL (37)

<sup>d</sup>Not originally identified in (30)

Table S2. Oxidatively Modified Residues in the D1, D2, CP43, and CP47 Proteins with 4 sec Irradiation. Individual residues are listed along with the modifications observed. In some instances, different modifications were observed for the same residue on different peptides. Key: aa, aldehyde addition (-32 amu); ca, carbonyl addition (+14 amu); cysh, cysteine hydroxyl (-16 amu); gam, Glu/Asp modification (-30 amu); go, general oxidation (+16 amu); stcb, serine/threonine carbonyl (-2 amu).

### Modified Protein Residues

**D1**  $^2\text{T}^{\text{a}}$  + stcb,  $^4\text{I}^{\text{a}}$  + go,  $^5\text{L}^{\text{a}}$  + go,  $^6\text{E}^{\text{a}}$  + gam,  $^7\text{R}^{\text{a}}$  + go,  $^{239}\text{F}$  + go,  $^{241}\text{Q}$  + ca,  $^{242}\text{E}$  + gam

**D2**  $^{18}\text{S}^{\text{c}}$  + go,  $^{19}\text{M}$  + aa,  $^{20}\text{D}$  + go,  $^{22}\text{W}$  + go,  $^{132}\text{E}$  + gam,  $^{133}\text{L}^{\text{c}}$  + ca,  $^{135}\text{R}$  + go,  $^{238}\text{P}$  + ca,  $^{239}\text{T}$  + go,  $^{242}\text{E}$  + gam,  $^{247}\text{M}^{\text{c}}$  + go,  $^{321}\text{L}$  + go,  $^{324}\text{E}^{\text{c}}$  + ca,  $^{326}\text{I}^{\text{c}}$  + go,  $^{330}\text{M}$  + go,  $^{338}\text{E}$  + gam,  $^{339}\text{N}$  + go,  $^{340}\text{L}$  + ca

**CP43**  $^{27}\text{D}$  + go,  $^{28}\text{Q}$  + ca,  $^{29}\text{E}$  + gam,  $^{212}\text{C}$  + do,  $^{213}\text{L}$  + ca,  $^{214}\text{L}$  + ca,  $^{215}\text{K}$  + ca,  $^{354}\text{E}^{\text{c}}$  + gam,  $^{355}\text{T}^{\text{c}}$  + go,  $^{356}\text{M}^{\text{c}}$  + aa or go,  $^{357}\text{R}^{\text{c}}$  + aa or go,  $^{365}\text{W}$  + go,  $^{367}\text{E}$  + gam,  $^{368}\text{P}$  + go or ca,  $^{369}\text{L}$  + go,  $^{370}\text{R}$  + ca,  $^{393}\text{A}$  + go,  $^{394}\text{E}$  + go,  $^{396}\text{M}$  + aa,  $^{459}\text{I}^{\text{c}}$  + go,  $^{460}\text{D}$  + go or gam,  $^{461}\text{R}$  + ca,  $^{462}\text{D}$  + gam or ca,  $^{464}\text{E}$  + gam,  $^{465}\text{P}$  + ca,  $^{466}\text{V}$  + go,  $^{467}\text{L}$  + ca,  $^{469}\text{M}$  + go or gam

**CP47**  $^{60}\text{M}$  + go,  $^{68}\text{R}^{\text{c}}$  + go,  $^{133}\text{L}^{\text{b}}$  + go,  $^{134}\text{D}^{\text{c}}$  + gam,  $^{135}\text{L}^{\text{b}}$  + ca,  $^{327}\text{A}$  + go,  $^{329}\text{S}$  + go,  $^{359}\text{M}$  + aa,  $^{360}\text{P}$  + go,  $^{361}\text{T}$  + go,  $^{364}\text{E}^{\text{c}}$  + gam,  $^{366}\text{F}$  + go,  $^{423}\text{R}^{\text{c}}$  + ca,  $^{425}\text{A}$  + go,  $^{428}\text{E}$  + gam,  $^{484}\text{P}$  + gam,  $^{486}\text{L}$  + go

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<sup>a</sup>Not resolved in the *Thermosynechococcus vulcanus* structure (15)

<sup>b</sup>Buried residues not adjacent to cavities/channels identified using PYMOL (37)

<sup>c</sup>Buried residues adjacent to cavities/channels identified using PYMOL (37)

Table S3. Oxidatively Modified Residues in the D1, D2, CP43, and CP47 Proteins with 8 sec Irradiation.

Individual residues are listed along with the modifications observed. In some instances, different modifications were observed for the same residue on different peptides. For a complete list of oxidative modification types, the amino acids targeted, and mass modifications searched for in this study, see (34).

Key: aa, aldehyde addition (-32 amu); ca, carbonyl addition (+14 amu) cysh, cysteine hydroxyl (-16 amu); gad, Glu/Asp decarboxylation (-30 amu); go, general oxidation (+16 amu); stcb, serine/threonine carbonyl (-2 amu)

### Protein Modified Residues

**D1**  $^{10}\text{S}^{\text{a}}$  + go,  $^{11}\text{E}$  + gam,  $^{12}\text{S}$  + go,  $^{13}\text{L}$  + ca,  $^{16}\text{R}$  + ca,  $^{130}\text{E}^{\text{c}}$  + go,  $^{131}\text{W}^{\text{c}}$  + kyn,  $^{132}\text{E}^{\text{b}}$  + go,  $^{134}\text{S}^{\text{c}}$  + go,  $^{328}\text{M}^{\text{c}}$  + go,  $^{329}\text{E}^{\text{c}}$  + gam,  $^{330}\text{V}$  + ca,  $^{332}\text{H}^{\text{c}}$  + go,  $^{333}\text{E}^{\text{c}}$  + gam or go,  $^{334}\text{R}^{\text{c}}$  + ca

**D2**  $^{18}\text{S}^{\text{c}}$  + stcb,  $^{19}\text{M}$  + go or do,  $^{20}\text{D}$  + gam,  $^{238}\text{P}$  + ca,  $^{239}\text{T}$  + go,  $^{242}\text{E}$  + gam,  $^{247}\text{M}^{\text{c}}$  + go,  $^{248}\text{V}$  + go,  $^{268}\text{L}^{\text{c}}$  + ca,  $^{272}\text{M}^{\text{c}}$  + to,  $^{277}\text{V}^{\text{b}}$  + ca,  $^{308}\text{E}$  + go,  $^{311}\text{E}$  + ca,  $^{312}\text{F}$  + do,  $^{321}\text{L}$  + ca,  $^{326}\text{I}^{\text{c}}$  + go,  $^{327}\text{R}^{\text{c}}$  + am,  $^{328}\text{A}$  + go,  $^{329}\text{W}$  + do,  $^{330}\text{M}$  + go,  $^{336}\text{P}$  + ca or go,  $^{337}\text{H}$  + go,  $^{338}\text{E}$  + gam or go,  $^{339}\text{N}$  + go,  $^{340}\text{L}$  + go or ca,  $^{341}\text{I}$  + go

**CP43**  $^{3}\text{T}^{\text{a}}$  + stcb,  $^{4}\text{L}^{\text{a}}$  + ca,  $^{7}\text{L}^{\text{a}}$  + go,  $^{9}\text{R}^{\text{a}}$  + ca,  $^{195}\text{D}$  + gam,  $^{196}\text{V}$  + go,  $^{197}\text{R}$  + ca,  $^{212}\text{C}$  + do,  $^{213}\text{L}$  + ca,  $^{214}\text{L}$  + ca,  $^{215}\text{K}$  + ca,  $^{354}\text{E}^{\text{c}}$  + gam,  $^{355}\text{T}^{\text{c}}$  + go,  $^{356}\text{M}^{\text{c}}$  + aa,  $^{357}\text{R}^{\text{c}}$  + ca or go,  $^{395}\text{Y}$  + go,  $^{396}\text{M}$  + aa or go or to,  $^{403}\text{S}$  + go,  $^{459}\text{I}^{\text{c}}$  + go,  $^{460}\text{D}$  + gam,  $^{461}\text{R}$  + ca,  $^{462}\text{D}$  + do,  $^{464}\text{E}$  + gam,  $^{469}\text{M}$  + go

**CP47**  $^{1}\text{M}^{\text{a}}$  + go,  $^{5}\text{W}^{\text{c}}$  + do,  $^{7}\text{R}$  + go,  $^{58}\text{Q}$  + go,  $^{60}\text{M}$  + go,  $^{66}\text{M}^{\text{b}}$  + aa,  $^{67}\text{T}^{\text{b}}$  + go,  $^{68}\text{R}^{\text{b}}$  + go,  $^{274}\text{Q}$  + go,  $^{275}\text{W}$  + go,  $^{276}\text{D}$  + gam,  $^{277}\text{Q}$  + ca,  $^{313}\text{D}^{\text{c}}$  + gam,  $^{314}\text{Y}^{\text{c}}$  + go,  $^{315}\text{I}^{\text{c}}$  + ca,  $^{329}\text{S}$  + go,  $^{330}\text{M}^{\text{c}}$  + go,  $^{358}\text{R}$  + ca,  $^{359}\text{M}$  + aa,  $^{360}\text{P}$  + go,  $^{361}\text{T}$  + go,  $^{362}\text{F}^{\text{c}}$  + do,  $^{363}\text{F}^{\text{c}}$  + do,  $^{364}\text{E}^{\text{c}}$  + gam,  $^{374}\text{D}$  + gad,  $^{376}\text{I}$  + ca,  $^{377}\text{V}$  + go,  $^{378}\text{R}$  + ca or go,  $^{384}\text{R}$  + am,  $^{423}\text{R}^{\text{c}}$  + ca or go,  $^{424}\text{A}$  + ca,  $^{425}\text{Q}^{\text{c}}$  + go,  $^{426}\text{L}^{\text{c}}$  + ca,  $^{430}\text{F}$  + do,  $^{431}\text{E}$  + go,  $^{432}\text{L}$  + go,  $^{433}\text{D}$  + gam,  $^{434}\text{R}$  + ca,  $^{484}\text{P}$  + go,  $^{485}\text{D}$  + gam,  $^{486}\text{L}$  + ca,  $^{500}\text{D}$  + gam,  $^{501}\text{P}$  + go,  $^{503}\text{T}$  + go,  $^{504}\text{R}$  + am

<sup>a</sup>Not resolved in the *Thermosynechococcus vulcanus* structure (15)

<sup>b</sup>Buried residues not adjacent to cavities/channels identified using PYMOL (37)

<sup>c</sup>Buried residues adjacent to cavities/channels identified using PYMOL (37)

**Table S4.** Oxidatively Modified Residues in the D1, D2, CP43, and CP47 Proteins with 16 sec Irradiation. Individual residues are listed along with the modifications observed. In some instances, different modifications were observed for the same residue on different peptides. For a complete list of oxidative modification types, the amino acids targeted, and mass modifications searched for in this study, see (34). Key: aa, aldehyde addition (-32 amu); ca, carbonyl addition (+14 amu); cysh, cysteine hydroxyl (-16 amu); gad, Glu/Asp decarboxylation (-30 amu); go, general oxidation (+16 amu); stcb, serine/threonine carbonyl (-2 amu).

### Modified Protein Residues

<b>D1</b>	$^2\text{T}^{\text{a}}$ + stcb, $^4\text{I}^{\text{a}}$ + go, $^6\text{E}^{\text{a}}$ + gam, $^7\text{R}$ + go, $^8\text{R}^{\text{a}}$ + go or ca, $^9\text{E}^{\text{a}}$ + gam, $^{10}\text{S}^{\text{a}}$ + go or stcb, $^{18}\text{C}$ + comc, $^{130}\text{E}^{\text{b}}$ + go, $^{131}\text{W}^{\text{b}}$ + kyn, $^{132}\text{E}^{\text{b}}$ + ca or gam, $^{133}\text{L}$ + go, $^{239}\text{F}^{\text{b}}$ + go, $^{241}\text{Q}^{\text{b}}$ + ca, $^{242}\text{E}^{\text{b}}$ + gam, $^{316}\text{T}$ + go, $^{319}\text{D}$ + gam, $^{320}\text{I}$ + ca, $^{328}\text{M}$ + go, $^{329}\text{E}^{\text{b}}$ + go, $^{330}\text{V}$ + ca, $^{331}\text{M}$ + go or do or to, $^{332}\text{H}$ + hro3 or oxhw, $^{333}\text{E}$ + gam,
<b>D2</b>	$^3\text{I}$ + ca, $^7\text{K}$ + ca, $^{10}\text{T}$ + ca, $^{11}\text{D}$ + go, $^{12}\text{E}$ + gam, $^{13}\text{K}$ + ca or go, $^{14}\text{D}$ + gad, $^{15}\text{L}$ + ca, $^{16}\text{F}$ + go, $^{18}\text{S}$ + go or stcb, $^{19}\text{M}$ + go or aa or do, $^{20}\text{D}$ + go or gad, $^{23}\text{L}$ + go, $^{132}\text{E}$ + gam, $^{133}\text{L}$ + ca or go, $^{134}\text{A}$ + go, $^{135}\text{R}$ + go, $^{238}\text{P}$ + ca, $^{239}\text{T}$ + go, $^{242}\text{E}$ + gam, $^{247}\text{M}$ + go, $^{248}\text{V}$ + go, $^{302}\text{Q}$ + ca, $^{303}\text{E}$ + go, $^{304}\text{I}$ + go, $^{321}\text{L}$ + ca, $^{324}\text{E}$ + gam, $^{326}\text{I}$ + ca, $^{327}\text{R}$ + go, $^{328}\text{A}$ + go, $^{329}\text{W}$ + do, $^{330}\text{M}$ + aa or go, $^{334}\text{D}$ + gam or go, $^{335}\text{Q}$ + go, $^{336}\text{P}$ + ca or go, $^{337}\text{H}$ + hro3, $^{338}\text{E}$ + gam or ca, $^{340}\text{L}$ + ca or go
<b>CP43</b>	$^{27}\text{D}$ + ca or go, $^{28}\text{Q}$ + ca or go, $^{29}\text{E}$ + gam or go, $^{195}\text{D}$ + gam, $^{196}\text{V}$ + ca or go, $^{197}\text{R}$ + ca or go, $^{212}\text{C}$ + do, $^{213}\text{L}$ + ca, $^{214}\text{L}$ + ca, $^{215}\text{K}$ + ca, $^{343}\text{R}^{\text{c}}$ + ca, $^{345}\text{P}$ + ca, $^{346}\text{T}$ + go, $^{348}\text{E}^{\text{b}}$ + gam, $^{354}\text{E}^{\text{c}}$ + ca or gam, $^{355}\text{T}^{\text{c}}$ + go, $^{356}\text{M}^{\text{c}}$ + aa or go, $^{357}\text{R}^{\text{c}}$ + am or ca or go, $^{359}\text{W}$ + kyn, $^{361}\text{L}^{\text{c}}$ + go, $^{362}\text{R}$ + am, $^{363}\text{A}^{\text{b}}$ + go, $^{364}\text{P}$ + go, $^{365}\text{W}$ + do, $^{366}\text{L}$ + ca or go, $^{367}\text{E}$ + gam, $^{368}\text{P}$ + ca or go, $^{369}\text{L}$ + ca, $^{370}\text{R}$ + ca, $^{376}\text{D}$ + gam, $^{383}\text{D}$ + gam, $^{384}\text{I}$ + go, $^{385}\text{Q}$ + ca or go, $^{387}\text{W}$ + do, $^{389}\text{E}^{\text{c}}$ + gam, R $^{391}$ + ca, $^{392}\text{A}$ + go or stcb, $^{394}\text{E}$ + gam or go, $^{395}\text{Y}$ + go, $^{396}\text{M}$ + aa, $^{397}\text{T}$ + go, $^{398}\text{H}$ + go, $^{400}\text{P}^{\text{c}}$ + ca, $^{459}\text{I}^{\text{c}}$ + go, $^{460}\text{D}$ + ca gam, $^{461}\text{R}$ + ca, $^{462}\text{D}$ + go, $^{463}\text{F}$ + ca, $^{464}\text{E}$ + ca or gam, $^{465}\text{P}$ + ca, $^{466}\text{V}$ + go, $^{469}\text{M}$ + go, $^{473}\text{N}$ + go
<b>CP47</b>	$^{60}\text{M}$ + go, $^{65}\text{F}^{\text{b}}$ + do, $^{66}\text{M}^{\text{b}}$ + aa or go, $^{133}\text{L}^{\text{b}}$ + ca or go, $^{134}\text{D}^{\text{c}}$ + gam, $^{135}\text{L}^{\text{b}}$ + ca or go, $^{137}\text{K}$ + ca, $^{274}\text{Q}$ + ca, $^{275}\text{W}$ + do or go, $^{276}\text{D}$ + gam or go, $^{287}\text{R}$ + ca, $^{289}\text{S}$ + go, $^{294}\text{E}$ + gam, $^{329}\text{S}$ + go, $^{330}\text{M}^{\text{c}}$ + go, $^{332}\text{N}$ + go, $^{334}\text{D}$ + gam, $^{336}\text{I}$ + ca, $^{358}\text{R}$ + ca or go, $^{359}\text{M}$ + aa, $^{360}\text{P}$ + go, $^{361}\text{T}$ + go or stcb, $^{362}\text{F}^{\text{c}}$ + go, $^{363}\text{F}^{\text{c}}$ + do, $^{364}\text{E}^{\text{c}}$

+ gam, <sup>365</sup>T<sup>c</sup> + go, <sup>374</sup>D + gam, <sup>376</sup>I + ca, <sup>377</sup>V + go, <sup>378</sup>R + go, <sup>393</sup>E + gam, <sup>394</sup>Q + ca, <sup>410</sup>S + stcb, <sup>411</sup>Y + do,  
<sup>413</sup>D + gam, <sup>423</sup>R<sup>c</sup> + ca, <sup>425</sup>Q<sup>c</sup> + go, <sup>426</sup>L<sup>c</sup> + go, <sup>428</sup>E + gam or go, <sup>429</sup>I + ca, <sup>430</sup>F + do, <sup>431</sup>E + ca or go, <sup>432</sup>L +  
go, <sup>433</sup>D + gam, <sup>434</sup>R + ca, <sup>439</sup>S+ stcb, <sup>484</sup>P + ca, <sup>485</sup>D + gam, <sup>486</sup>L + go, <sup>500</sup>D + gam, <sup>501</sup>P + ca + go, <sup>502</sup>T +  
go or stcb, <sup>503</sup>T + ca or go, <sup>504</sup>R + go

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<sup>a</sup>Not resolved in the *Thermosynechococcus vulcanus* structure (15)

<sup>b</sup>Buried residues not adjacent to cavities/channels identified using PYMOL (37)

<sup>c</sup>Buried residues adjacent to cavities/channels identified using PYMOL (37)